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Electrochemical Amination of Benzene in Aqueous-Acetic Solutions of Sulfuric Acid

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Abstract—Indirect cathodic amination of benzene with hydroxylamine in the presence of Ti(IV)/Ti(III) mediator system in aqueous media containing 4–11 mol/L H_2SO_4 and 13–5.5 mol/L AcOH has been studied. Aniline, diphenyl, and isomeric phenylenediamines are the electrolysis products at 25–60°C. The increase in temperature favors the formation of the monoamino compound. Aniline yield with respect to hydroxylamine at complete conversion of the latter has reached 78.7%, mass fraction of aniline being 97.1%.

Keywords: cathode, Ti(IV)/Ti(III) mediator system, hydroxylamine, benzene, cation-radical aromatic substitution, aniline

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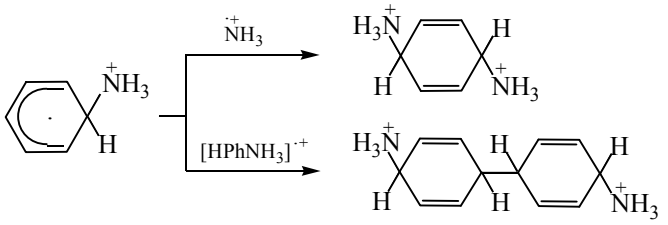
Indirect cathodic amination of aromatic substrates by the Ti(IV)–NH_2OH system is performed in media containing sulfuric acid and yields mono- and diamino compounds [1]; the increase in H_2SO_4 concentration favors the deeper substitution. Functionalization of the substrates poorly soluble in water can be more efficient if AcOH or MeCN (approach the maximum possble concentration) is used as the solvent in sulfuric acid-containing catholytes instead of water [1–3]. The addition of an organic solvent at constant concentration of H_2SO_4 has led to the increase in the total yield of amino compounds and the fraction of the monosubstituted products. For instance, using anisole amination in sulfuric acid-acetic acid media as the example, relatively mild conditions of preparation of monosubstituted products from the substrates activated with respect to amino cation-radicals have been elaborated [2]. Isomeric anisidines with overall current efficiency and yield with respect to hydroxylamine above 80% have been obtained at complete conversion of the source of amino radicals at 15–25°C in the catholyte containing 4 mol/L of H_2SO_4 and 13 mol/L of AcOH [2].

In this work, we investigated the amination of benzene to evaluate the possibility of the use of catholytes containing sulfuric and acetic acids to efficiently introduce a single amino group in the aromatic rings of non-activated substrates. A special feature of this process that the products of electrochemical [1, 4] and chemical [5–8] amination in weakly and moderately acidic media, alongside aniline, include unstable amino compounds formed via biradical reactions such as reactions (1) and (2) and, probably, in successive reactions of aminocyclohexadienyl cation-radical with benzene and the amino cation-radical, owing to insufficiently high oxidation potential of Ti(IV).



(1)

(2)